Renewable and Sustainable Energy Reviews 14 (2010) 1999–2008

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

High quality biodiesel and its diesel engine application: A review

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ARTICLE INFO

Article history:
Received 2 February 2010
Accepted 10 March 2010

Keywords:
Quality biodiesel
Purification technology
Feedstock
Higher lubricity
Biodegradability

ABSTRACT

The continuous increasing demand for energy and the diminishing tendency of petroleum resources has led to the search for alternative renewable and sustainable fuel. Biodiesel is best substitute for petro-diesel and also most advantageous over petro-diesel for its environmental friendliness. The quality of biodiesel fuel was found to be significant for its successful use on compression ignition engines and subsequent replacement of non-renewable fossil fuels. Conventional biodiesel separation and purification technologies were noticed to yield lower quality biodiesel fuel with resultant excessive energy and water consumptions. Membrane technology showed more potential for effective and efficient separation and purification of biodiesel. This technology need be explored for the attainment of better quality biodiesel fuels. This paper reviews the technologies used for the biodiesel separation and purification, biodiesel quality, and its effects on diesel engines. Biodiesel biodegradability, lubricity, stability, economic importance, and gaseous emissions have been discussed.

Contents

1. Introduction

The concept of biodiesel as an alternative diesel fuel has been gaining great importance worldwide for its good quality exhaust, sustainability and biodegradability. Biodiesel, referred to as mono-alkyl esters are derived from vegetable oils and animal fats, and alcohols of lower molecular weights in the presence of catalysts. Vegetable oils and animal fats are generally insoluble in water, and are commonly regarded as hydrophobic substances belonging to plant and animal kingdom consisting of one mole of glycerol and three moles of fatty acids [1]. Transesterification reaction is must adopted for the commercial production of biodiesel [1–6]. The reaction can be catalyze either using homogeneous catalysts (acid or base) or heterogeneous catalysts (acid, base, or enzyme). The use

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doi:10.1016/j.rser.2010.03.020

of homogeneous alkaline catalysts especially sodium and potassium hydroxides provide higher reaction rate and conversion than the acid catalysts for the transesterification of triglycerides to biodiesel. The problems of reversibility encounter in stepwise reactions for the production of biodiesel were overcome using higher molar ratios to shift the reaction to completion [7]. Homogeneous alkali-catalyzed transesterification reaction is about 4000 times faster than the homogeneous acid-catalyzed reaction [8]. The alkali (sodium and potassium hydroxides) catalysts are more popular and most preferred in the commercial production of biodiesel for their low cost and availability [9]. The application of heterogeneous catalysts such as solid metal oxide in the production of biodiesel to circumvent the problems of downstream purification is faced with elevated reaction temperatures and cost [10]. In the case of enzymatic catalysis, although the rates of triglycerides conversion to fatty acids alkyl esters are known to be slower, the application of the process is reasonable for the advantages of simplicity in the product refining process and the allowance for the use of lower reaction temperature [11]. One major problem with the use of enzymatic reactions for the production of biodiesel is the higher cost of enzymes [12]. Biodiesel production was intended to mainly address the issue of fuel supply security, but recently more attention has been centred on the use of renewable fuels in order to minimize the overall net production of carbon-dioxide (CO_2) from non-renewable fossil fuel combustion. Furthermore, biodiesel does not increase green house gas levels in the atmosphere because of its closed cycle. In other word it is said to be carbon neutral, as biodiesel yielding plants take away more carbon-dioxide than that contributed to the atmosphere when used as source of energy [13]. However, in a life cycle analysis the overall carbon-dioxide emission was calculated to be decreased by 78% when biodiesel was used as fuel compared to the mineral diesel [5].

The major drawbacks inhibiting commercial production of biodiesel include the cost of raw materials and the presence of free fatty acids, water in the oils and the use of higher alcohol molar ratios. The presence of water molecules reduces the catalytic effectiveness while free fatty acids lead to the formation of soap when alkali catalyst is used during transesterification reaction. This process decreases the yields of esters and renders purification of crude biodiesel difficult and expensive. The production of soap, sometimes called alkaline hydrolysis, converts trialcylglycerols to glycerol and form a mixture of salts of long chain carboxylic acids. Apart from the soap formation, other smaller contaminants present in crude biodiesel due to reversibility include amongst others; mono-, di-, and triglycerides and glycerol, etc. The purity and quality of biodiesel is determined by the amounts of free and bonded glycerine. Combustion of these substances in compression ignition engines can enhance the formation of undesirable substances such as acrolein, a photochemical smog ingredient [14]. To get rid of these contaminants several different conventional or traditional separation and purification techniques such as gravitational settling, distillation, evaporation, washing with water, acid, absorbent have been employed to ensure the achievement of highly purified and quality biodiesel. Most notable improved techniques being used are the membrane reactor and separative membrane for the removal of these by-products from biodiesel mixture.

The application of membrane technology in the separation and purification of biodiesel has tremendously reduced water washing application, and have saved a reasonable amount of time and energy consumption. Highly purified biodiesel is necessary to achieve the stringent ASTM-D-6751-03 and EN-14214 standard of biodiesel specifications. Production of high quality biodiesel can undoubtedly minimize or erase on the map, the problems of ring sticking, coking and trumpet formation on the injectors, carbon deposits, and thickening and gelling of lubricating oils effects, and also enhance the performance of the diesel engines. The use of biodiesel in diesel engines reduces the emissions of hydrocarbons, carbon monoxide, particulate matter, and sulfur dioxide [15]. Only nitrogen oxide emission increases: this behaviour is due to the oxygen content of biodiesel [13]. This paper reviews the concept of biodiesel purity, quality and its application in diesel engines.

2. Biodiesel purification technologies

The purification of the crude biodiesel can be technically and most often difficult contributing to the increase in biodiesel production cost. The purity of biodiesel must be high and generally have to conform to the international biodiesel standard specifications provided by American standard for testing materials (ASTM) and European Union (EU) standards for alternative fuels. According to the European Union (EU) standard specifications for biodiesel fuel water content, free fatty acids, and free and bound glycerine, must be kept to a minimum level and the purity of the fuel must exceeds 96.5% [16]. The crude products of transesterification reaction consist mainly of fatty acid alkyl ester (biodiesel), and other secondary products such as soap, diglycerides, monoglycerides, glycerol, alcohol, and catalyst, etc. in different concentration levels. The main objective in the purification of crude biodiesel is to remove the fatty acid alkyl esters from the mixture, and maintain lower cost of production and also ensure a highly purified biodiesel product. Glycerol, considered as a major secondary product of the transesterification reaction in its purest form can be sold to various commercial manufacturing industries such as cosmetic, food, tobacco and pharmaceutical industries, etc. for different applications. In order to make biodiesel production cost effective removal and resale of glycerol is mandatory. The remaining product mixtures containing other by-products such as alcohols also need to be recovered through either distillation or evaporation process. However achievement of high conversion rate results in the immediate formation of distinct two liquid phases, with also sharp solid phase when heterogeneous catalyst is employed. The bottom phase of the products consists of glycerol and the upper phase contains fatty acid alkyl esters and alcohol. For cases where by the reaction could not attain complete conversion the unreacted triglycerides and bound glycerol will form solid substance at the bottom phase posing severe difficulty in the separation and purification of crude fatty acid alkyl esters. Kusdiana and Saka [17] reported that a higher molar ratio of alcohols to vegetable oils greater than 5.67 creates a lot of difficulties in the separation of glycerol from methanol. Refined vegetable oils tend to ease the difficulties encountered during separation and purification of the transesterified products (biodiesel) and provide biodiesel with better physicochemical properties such as viscosity, flash point and densities, etc. However the use of unrefined vegetable oils as raw materials in the production of biodiesel poses great difficulty in the purification processes, leading to low quality biodiesel fuel. Casimir et al. [18] stated that poor-quality vegetable oils may inactivate the basic catalysts or even enzyme catalysts, lowering the yield and rendering purification and isolation of fatty acid methyl esters (biodiesel) difficult. Lin et al. [19] investigated bench-scale degumming of crude vegetable oil. The authors stated that crude vegetable oils contain various minor contaminants such as phospholipids, colouring pigments, waxes, and free fatty acids (FFAs) that may affect the quality of the finished oils. Membrane technology was used to purify the crude vegetable oils for further application such as production of biodiesel fuel. Crude vegetable oil membrane refining provides high purity and quality oils [20]. Srivastava and Verma [21] reported that vegetable oil moisture content was removed by subjecting the oil to a temperature of 110 °C in an oven for 1 h before starting the transesterification

Table 1
Comparisons of different biodiesel separation and purification technologies.

Type of catalyst	Separation method	Purification method	Application(s)	Drawback(s)	References
1. Solid oxide.	Gravitational settling.	Evaporation.	Removal of methanol.	Less energy consumption.	Gerard et al. [23].
2. Sodium hydroxide.	Microwave irradiation.	Water washing.	Removal of excess methanol and catalyst.	Water washing suffers from large amount of water-waste and energy consumption.	Saifuddin and Chua [24].
3. Sodium methoxide.	Centrifugation.	Distillation/neutralization/ water washing.	Methanol recovery, removal of excess methanol and catalyst.	Energy and water waste.	Michael et al. [25].
4. Sodium hydroxide.	Gravitational settling.	Neutralization with acid/ warm water washing.	Removal of methanol, residual catalyst and soap.	High energy and water consumption.	Tint and Mya [26].
5. Acid/potassium hydroxide.	Centrifugation.	Washing with hot distilled water.	Removal of residual methanol and other contaminants.	High water and energy consumption.	Bugaje and Mohammed [27].
6. Sodium hydroxide.	Membrane filtration.	Neutralization/membrane/ water washing.	Removal of excess methanol, residual catalyst and soap.	Less water, time and energy waste.	Low and Cheong [28].
7. Enzyme/acid.	Gravitational settling.	Evaporation.	Removal of excess methanol.	Less water waste.	Wei-Jia et al. [29].
8. Sodium hydroxide.	Membrane reactor/ separatory funnel.	Washing with reverse osmosis water.	Removal of unreacted oil, traces soap.	Less water requirement.	Dube et al. [30].
9. Potassium hydroxide.	Separative membrane.	Separative membrane.	Removal of excess methanol and soap.	No waste water.	Yong et al. [31].
10. Sodium hydroxide.	Membrane separator.	Membrane separator.	Removal of unreacted tri- and mono-glycerides and glycerol.	No water requirement.	Tremblay et al. [32].
11. Sodium methoxide.	Separatory funnel.	Neutralization/distilled water washing/distillation.	Removal of contaminants.	High water waste and energy consumption.	Fangrui et al. [33].

reaction. They stated that for effective use of vegetable oils as raw materials for the production of biodiesel, both free fatty acids and the water level must fall within the stipulated standard specification. Free fatty acid must fall within 0.5–3% while and the water content to be less than 0.6%, respectively. Mushtaq et al. [22] reported that the yields of esters are significantly reduced if the raw materials requirements for the production of biodiesel are not achieved. Table 1 shows comparisons between different separation and purification technologies.

3. High quality biodiesel

The major focal point for biodiesel high quality is the adherence to biodiesel standard specifications. These standard specifications could either be the American standards for testing materials (ASTM 6751-3) or the European Union (EN 14214) for biodiesel fuel. The technologies applied to refine the feedstock and convert it to fatty acid alkyl esters (biodiesel) determine whether the fuel produced will meet the designed specification standards. The purity and quality of biodiesel fuel can be significantly influenced by numerous factors amongst others include: the quality of feedstock, fatty acid composition of the vegetable oils (virgin oils), animal fats and waste oils, type of production and refining process employed and post-production parameters. Tables 2 and 3 show the international standards specification of biodiesel fuel.

Table 2
Bio-diesel, B100, specification-ASTM-D-6751-06 [34].

Property	ASTM method	Limits	Units
Flash point	D93	130 min	°C
Water and sediment	D2709	0.050 max	vol.%
Kinematic viscosity, 40 °C	D445	1.9–6.0	mm^2/s
Sulfated ash	D874	0.020 max	mass%
Sulfur	D5453	–	–
S 15 grade	–	15 max	ppm
S 500 grade	–	500 max	–
Copper strip corrosion	D130	No. 3 max	–
Cetane	D613	47 min	–
Cloud point	D2500	Report	°C
Carbon residue 100% sample	D4530[a]	0.050 max	mass%
Acid number	D664	0.50 max	mg KOH/g
Free glycerine	D6584	0.020 max	mass%
Total glycerine	D6584	0.240 max	mass%
Phosphorus content	D4951	0.001 max	mass%
Distillation temperature, atmospheric equivalent temperature, 90% recovered	D1160	360 max	°C
Sodium/potassium	UOP391	5 max combined	ppm

[a] The carbon residue shall be run on the 100% sample.

3.1. Feedstock quality

Raw materials contribute to a major portion in the cost of biodiesel production, and are classified principally into three: vegetable oils, waste cooking oils and animal fats. Vegetable oils can be edible such as cottonseed, groundnut, corn, rapeseed, soybean, palm oil, sunflower, peanut, coconut, etc. and non-edible such as jatropha, pongamia, neem, rubber seed, mahua, silk cotton tree, jojoba, and castor oil. However animal fats may of the following form; tallow, lard, and yellow grease, etc. The degree of refining of the feedstock contributes a lot in the determination of the purity and high yield of biodiesel. Van Gerpen [36] reported that analysis of crude and refined vegetable oils as feedstock in the production of biodiesel indicated yield reduction of methyl esters from 93% to 98% for refined oil to 67% to 86% for crude oil. This was attributed mostly to the presence of up to 6.66% free fatty acids in the crude oil, although phospholipids were also suggested as a source of catalyst destruction. Vegetable oils, animal fats, or greases naturally contains free fatty acids (FFAs) referred to as saturated or unsaturated monocarboxylic acids but are not attached to glycerol backbones [37]. Higher amount of free fatty acids leads to higher acid value. Vegetable oils should have free fatty acids within a desired limit for homogeneous alkaline catalyzed transesterification reaction to occur, beyond which either the reaction will not take place or the yield will be too low. Table 4 depicts the level of FFA worked out by researchers. It is obviously clear from Table 4 that the free fatty acid level in the vegetable oil should be below a desired level (ranging from less than 0.5% to less than 3%) for alkaline transesterification reaction to occur. Michael [4] reported that vegetable oils suitable for use as a feedstock for biodiesel production should have water content lower than 0.06%. Furthermore, the transesterified product obtained from such oils could be easily refined without much separation and purification difficulties.

Table 3
International standard (EN 14214) requirements for biodiesel [35].

Property	Units	Lower limit	Upper limit	Test-method
Ester content	% (m/m)	96.5	–	Pr EN 14103 d
Density at 15 °C	kg/m^3	860	900	EN ISO 3675/EN ISO 12185
Viscosity at 40 °C	mm^2/s	3.5	5.0	EN ISO 3104
Flash point	C	>101	–	ISO CD 3679e
Sulfur content	mg/kg	–	10	–
Tar remnant (at 10% distillation remnant)	% (m/m)	–	0.3	EN ISO 10370
Cetane number	–	51.0	–	EN ISO 5165
Sulfated ash content	% (m/m)	–	0.02	ISO 3987
Water content	mg/kg	–	500	EN ISO 12937
Total contamination	mg/kg	–	24	EN 12662
Copper band corrosion (3 h at 50 °C)	rating	Class 1	Class 1	EN ISO 2160
Oxidation stability at 110 °C	h	6	–	pr EN 14112 k
Acid value	mg KOH/g	–	0.5	pr EN 14104
Iodine value	–	–	120	pr EN 14111
Linoleic acid methyl ester	% (m/m)	–	12	pr EN 14103d
Polyunsaturated (P4 double bonds) methylester	% (m/m)	–	1	–
Methanol content	% (m/m)	–	0.2	pr EN 141101
Monoglyceride content	% (m/m)	–	0.8	pr EN 14105m
Diglyceride content	% (m/m)	–	0.2	pr EN 14105m
Triglyceride content	% (m/m)	–	0.2	pr EN 14105m
Free glycerine	% (m/m)	–	0.02	pr EN 14105m/pr EN 14106
Total glycerine	% (m/m)	–	0.25	pr EN 14105m
Alkali metals (Na + K)	mg/kg	–	5	pr EN 14108/pr EN 14109
Phosphorus content	mg/kg	–	10	pr EN14107p

3.2. Fatty acid composition of vegetable oil

Natural vegetable oils and animal fats are processed to obtain crude oil or fat. These oils or fats normally contain sterols, phospholipids, free fatty acid, and water, odourants and other contaminants. However, even refined oils and fats contain small of amount of free fatty acid and water. Free fatty acid and water contents affect the transesterification reaction of triglycerides and also interfere with the separation and purification of fatty acid alkyl esters from other impurities thereby affecting the quality and yield of the final biodiesel products. Table 5 shows the composition of some notable vegetable oils and fats.

3.3. Production of biodiesel and refining process

The technologies involved in the production of biodiesel are classified into the following: direct use and blending, microemulsion, pyrolysis and transesterification. The most commonly used technology is the transesterification reaction of vegetable oils and animal fats with alcohol in the presence of catalyst [1,47,48]. This technology is most favoured in the commercial biodiesel production especially with the use of alkaline catalyst such as potassium and sodium hydroxide [43,49,50]. The introduction of membrane reactor for the transesterification of vegetable oil and the use of separative membrane in the crude biodiesel refining process have significantly reduced biodiesel production and purification difficulties and have also maintained the advantages of short reaction time, low reaction temperature, higher yield, direct conversion process, and simplicity in operation. Crude biodiesel contains a number of contaminants of different concentration levels. To achieve high quality biodiesel final product, down-stream process treatment is required. Biodiesel after refining must contain water lower than a maximum value of 0.050% (v/v) to meet ASTM biodiesel standard specification [25]. Figs. 1 and 2 compare conventional and membrane biodiesel production and purification processes.

Dube et al. [30] discussed the separation and purification difficulties often encountered when conventional technologies are employed in the production of biodiesel. The authors used membrane reactor to circumvent these difficulties, and achieved more purified and high quality biodiesel. The application of membrane technology especially ceramic membranes in the production and treatment of down-stream products, as shown in Fig. 2 offers several advantages over conventional technologies amongst others include: methanol recycling, quality product, less energy and little water consumption, application of waste oils and less soap formations.

Table 4
Amount of free fatty acid regulation for transesterification reaction.

Author	FFA (%)	Reference
Michael	<1	[4]
Ma and Hanna	<1	[1]
Harding et al.	<0.5	[11]
Ramadhas et al.	≤2	[38]
Gan et al.	<0.5	[39]
Canakci and Van Gerpan	<3	[40]
Zhang et al.	<0.5	[41]
Freedman et al.	<1	[42]
Nestor et al.	<0.5	[43]
Tiwari et al.	<1	[44]
Sahoo et al.	≤2	[45]
Sharma et al.	≤2	[46]

4. Biodiesel as diesel engine fuel

Biodiesel is an important alternative vehicular fuel. It has excellent properties as diesel engine fuel, so it can be used in compression-ignition diesel engines [15,39,51–55]. Biodiesel can be derived from several different vegetable oils or animal fats feedstock. Vegetable oil and animal fat direct use as fuel in diesel engines is limited due to two main factors; low volatility and high viscosity [56]. Traditional processing involves an alkali-catalyzed process, but this process is difficult for lower cost high free fatty acid feedstock due to soap formation. Pretreatment of the feedstock with high free fatty acid using strong homogeneous acid catalysts such as sulfuric acid have been shown to provide reasonable conversion rate, higher yields and high quality biodiesel final products. These technologies have played a vital role in ensuring the production of biodiesel from feedstock like soap-stock that are normally regarded as waste. Biodiesel is now

Table 5
Typical fatty acid composition-common oil source Fangrui and Hanna [1].

Fatty acid	Soybean (wt.%)	Beef tallow (wt.%)	Coconut (wt.%)	Palm (wt.%)	Lard (wt.%)	Cottonseed (wt.%)
Lauric	0.1	0.1	46.5	0.1	0.1	0.1
Myristic	0.1	2.8	19.2	1.0	1.4	0.7
Palmitic	10.2	23.3	9.8	42.8	23.6	20.1
Stearic	3.7	19.4	3	4.5	14.2	2.6
Oleic	22.8	42.4	6.9	40.5	44.2	19.2
Linoleic	53.7	2.9	2.2	10.1	10.7	55.2
Linolenic	8.6	0.9	0	0.2	0.4	0.6

mainly being produced from rapeseed, cottonseed, soybean, canola and palm oils [57]. Demirbas [58] stated that the higher heating values (HHVs) of biodiesels are relatively high. The values of HHVs of biodiesels ranged from 39 to 41 MJ/kg and are slightly lower when compared those of gasoline (46 MJ/kg), petro-diesel (43 MJ/kg), or petroleum (42 MJ/kg), but greater than coal (32–37 MJ/kg). Ejaz and Younis [59] reviewed biodiesel as vehicular fuel. The authors concluded that almost all types of vegetable oils can be used to replace the diesel oil; however the rapeseed oil and palm oil can be the most suitable vegetable oils which can be used as diesel fuel, additive or diesel fuel extender. Biodiesel termed as clean fuel does not contain carcinogenic substances and its sulfur content level is also lower than its content in petro-diesel. The ability of biodiesel to be highly biodegradable and its superb lubricating property when used in compression ignition engines makes it to be an excellent fuel. Also its renewability and similarities in physicochemical properties to petro-diesel, revealed its potentials and practical usability as fuel for the replacement of petro-diesel in the nearest future. Kegl [60] reported that few other physical and chemical properties of biodiesel fuel are of great concern and require to be enhanced to make it fit for use in clean form (i.e. 100% biodiesel). These properties include among others;

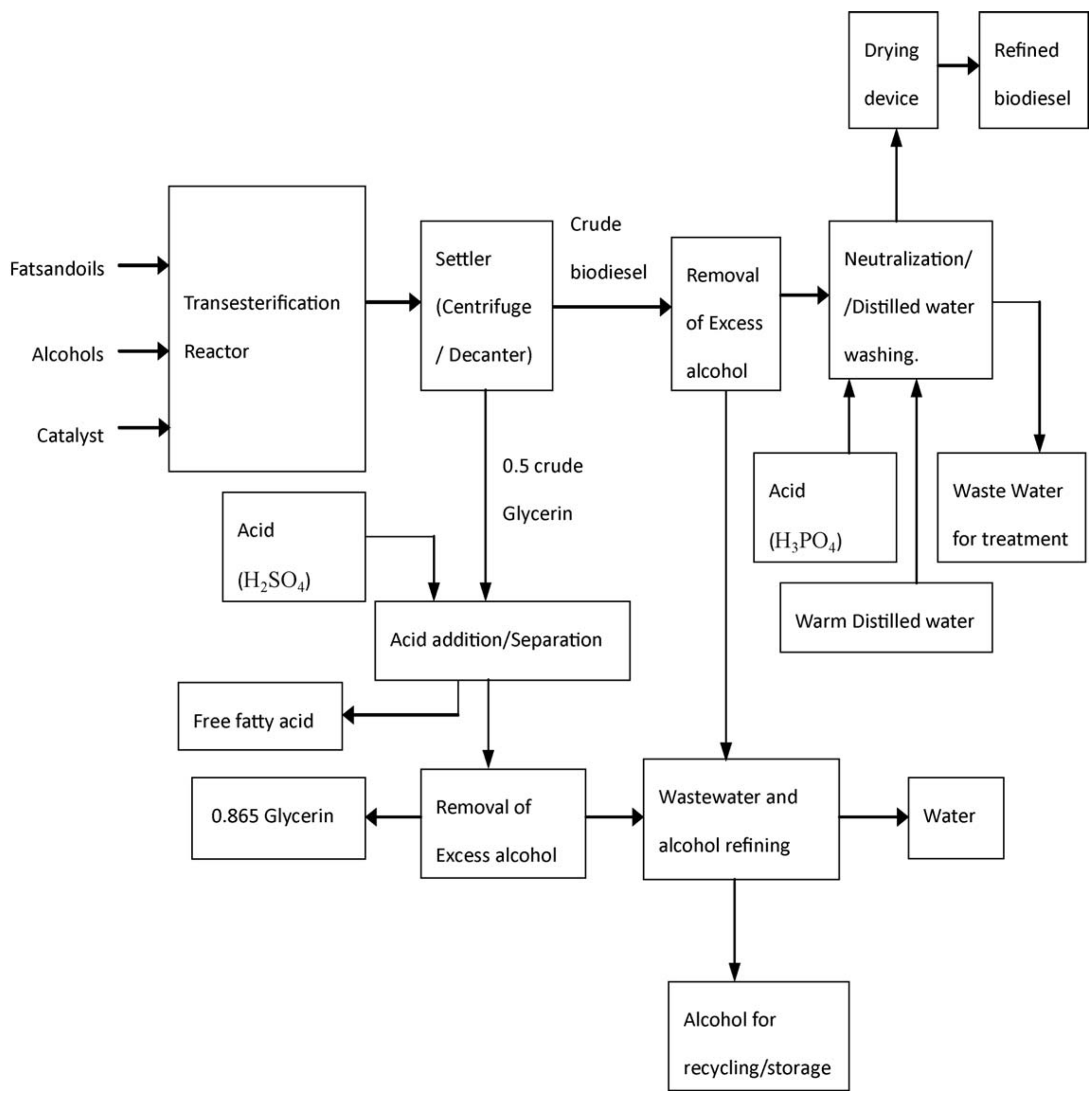

Fig. 1. Conventional biodiesel production and purification.

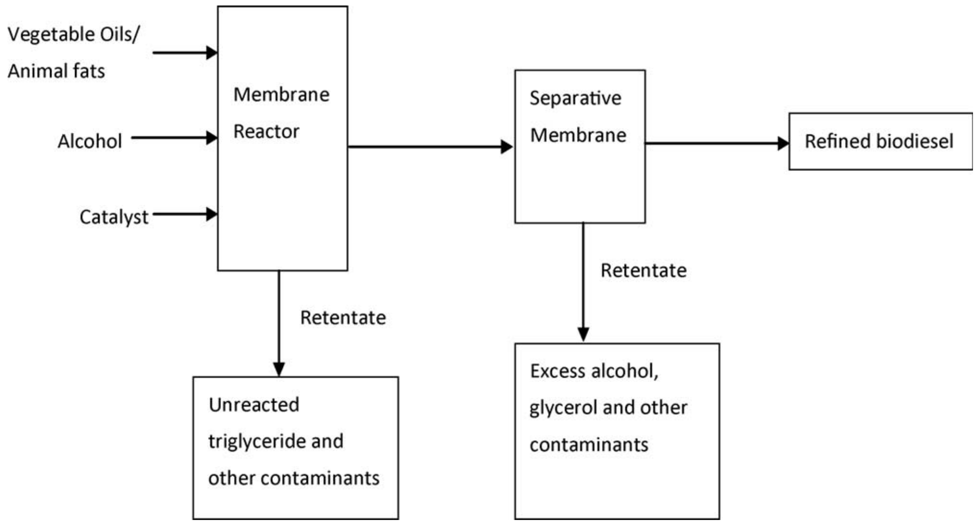

Fig. 2. Biodiesel production and purification using membrane technology.

engine power, increase in calorific value, reduced emission of nitrogen oxides (NO*x*), and low temperature properties improvement. Demirbas [35] reported that methyl esters improve the lubrication properties of the diesel fuel blend. Biodiesel decrease long term engine wear in compression ignition engines. Biodiesel is a good lubricant and is about 66% better than petro-diesel. Its oxidation stability improvement is also important to prevent it from deteriorating when stored over time. Currently biodiesel is compatible in blended form with petro-diesel in the ratio 20 (biodiesel): 80 (mineral diesel). Biodiesel has also being in use in many countries such as United States of America, Malaysia, Indonesia, Brazil, Germany, France, Italy and other European nations [33,37].

Biodiesel as an alternative to diesel fuel could only be successfully used in compression-ignition diesel engines, if its physical and chemical properties conform to the international standard specifications of biodiesel. These standards (ASTM 6571-3, EN 14214) describe the minimum requirement that must be met before biodiesel is used as a pure fuel or blended with petroleum-based diesel fuel. Biodiesel fuels are characterized by their cetane number, density, viscosity, cloud and pour points, flash point, copper corrosion, ash content, distillation range, sulfur content, carbon residue, acid value, free glycerine content, total glycerine content and higher heating value (HHV), etc. The viscosity values of vegetable oils decreases sharply after transesterification reaction [46]. Demirbas [35] stated that the flash point values of fatty acid methyl esters are significantly lower than those of vegetable oils. The author reported high regression between the density and viscosity values of vegetable oil methyl esters and a considerable regular relationship between viscosity and flash point of vegetable oil methyl esters. The relatively higher flash point of biodiesel to petro-diesel makes it a safer fuel to use, handle and store. Dube et al. [30] stated that biodiesel is an ideal fuel for use in sensitive environments, such as marine areas, national parks and forests, and heavily polluted cities for its relatively low emission profile.

4.1. Physicochemical properties of biodiesel fuels

The physicochemical properties of biodiesel are similar to those of petro-diesel fuels. Beg et al. [61] reported that viscosity is the most valuable property of biodiesel fuels since it has tremendous effects on the operation of fuel injection equipment, particularly at lower temperatures where an increase in viscosity affects the fluidity of the fuel. It was also stated that higher viscosity leads to poorer atomization of the fuel spray and which affects accuracy of the operation of fuel injectors. However the lower the viscosity of the biodiesel, the easier it is to pump, atomizes and achieves finer droplets [61]. Saka and Isayama [62] revealed kinematic viscosity to be an index which measures fuel stickiness, better viscosity values inhibit nebulization of fuel in the ignition chamber, poor values hamper the engine lubrication effects, hence, the viscosity values of the biodiesel must be kept within the stipulation range of international standard specification. Transesterification reaction converts triglycerides into methyl or ethyl esters and reduces the molecular weight to one third that of the triglyceride and decreases the viscosity of vegetable oils by a factor of about eight [33]. The viscosities of biodiesel fuel from animal fats such as lard and tallow show the same trends as temperatures, higher than the soybean and rapeseed biodiesel fuels. Virgin and waste vegetable oils can be used as fuel for compression ignition engines, but their viscosity is much higher than that of common diesel fuels and this requires major diesel engines modifications. Gunvachai et al. [5] reported the burning of vegetable oils in diesel engines is not clean resulting to the formation of wanted materials such as acrolein and organic acid. These materials lead to significant negative effects on the performance and longitudinal engine durability. However vegetable oils can be converted into their fatty acid methyl esters by transesterification reaction and can be convertibly used as fuels for diesel engine applications without major modifications [35]. Table 6 summarizes the physicochemical properties of main biodiesel fuels.

4.2. Biodegradability of biodiesel

Biodegradability of biodiesel has been considered to be a solution for waste accumulation leading to environmental pollution. Demirbas [63] stated that biodegradable fuels such as biodiesels have a wide range of potential applications and they are environmentally friendly. The author revealed that there is growing interest in degradable diesel fuels that degrade faster than the traditional disposable fuels. It was stated that biodiesel is non-toxic and degrades about four times faster than petro-diesel. Also its oxygen content improves the biodegradation process [58]. Ferella et al. [13] reported that biodiesel highly biodegradable in soil so also in fresh water. They also stated that under either aerobic or anaerobic prevailing conditions the most important part of biodiesel is degraded within 21–28 days. Tian et al. [3] reported that biodiesel biodegradability provides numerous positive

Table 6
Physicochemical properties of biodiesel fuels Hideki et al. [65].

Vegetable oil methyl ester	Kinematic viscosity (mm^2/s)	Cetane number	Lower heating value (MJ/l)	Cloud point (°C)	Flash point (°C)	Density (g/l)	Sulfur (wt.%)
Peanut	4.9 (37.8 °C)	54	33.6	5	176	0.883	–
Soybean	4.5 (37.8 °C)	45	33.5	1	178	0.885	–
Soybean	4.0 (40 °C)	45.7–56	32.7	–	–	0.880 (15 °C)	–
Babassu	3.6 (37.8 °C)	63	31.8	4	127	0.879	–
Palm	5.7 (37.8 °C)	62	33.5	13	164	0.880	–
Palm	4.3–4.5 (40 °C)	64.3–70	32.4	–	–	0.872–0.877 (15 °C)	–
Sunflower	4.6 (37.8 °C)	49	33.5	1	183	0.860	–
Tallow	–	–	–	12	96	–	–
Rapessed	4.2 (40 °C)	51–59.7	32.8	–	–	0.882 (15 °C)	–
Used rapeseed	9.48 (30 °C)	53	36.7	–	192	0.895	0.002
Used corn oil	6.23 (30 °C)	63.9	42.3	–	166	0.884	0.0013
Diesel oil	12–3.5 (40 °C)	51	35.5	–	–	0.830–0.840 (15 °C)	–

contributions to the environment. Prafulla and Shuguang [64] reported biodiesel to be better than petro-diesel in terms biodegradability, free sulfur content, viscosity, density, flash point and aromatic content. Table 6 present physicochemical properties of biodiesel fuels.

4.3. Higher lubricity

Lapuerta et al. [66] reported that fatty acid alkyl esters (biodiesel) have improved lubrication characteristics, but they can contribute to the formation of deposits, plugging of filters, depending mainly on degradability, glycerol (and other impurities) content, cold flow properties, etc. This lubrication property help in improving the fuel injectors and fuel pumps lubrication capacity. Biodiesel reduced long term engine wear in test diesel engines to less than half of what was observed in engines running on current low sulfur diesel fuel. Demirbas [35] stated that biodiesel provides significant lubricity improvement over petro-diesel fuel. Lubricity results of biodiesel and petro-diesel using industry test methods indicate that there is a marked improvement in lubricity when biodiesel is added to conventional diesel fuel. The author reported that even biodiesel levels below 1% can provide up to a 30% increase in lubricity.

4.4. Stability of biodiesel

The oxidation and polymerization of biodiesel fuel during combustion and storage is major concern in terms of the quality of biodiesel. These problems lead biodiesel fuel to become acidic, form un-dissolvable gum and sediments that can plug fuel filters. However, oxidation and polymerization occurs due presence of unsaturated fatty acid chains and the double bond in the parent molecule, which immediately react with the oxygen as soon as it is being exposed to air. Kapilan et al. [67] reported that oxidation of fatty acid chains is a complex process that is followed by a variety of mechanisms. This oxidation process of biodiesel is influenced by several factors including; light, temperature, extraneous materials, peroxides, size of the surface area between biodiesel and air. The authors stated that one of the methods of improving biodiesel oxidative stability includes the deliberate addition of antioxidants or modification of the fatty ester profile.

4.5. Lower emissions of biodiesel

The use of millions of vehicles across the globe especially in big cities and towns contribute a lot in generating gaseous emissions, hence polluting the environment. These emissions referred to as green house gases are attributed to the cause of global warming. Green house gases such as carbon-dioxide, carbon monoxide, nitrogen oxide, and sulfur causes climatic distraction resulting in drought and environmental adversities on both fauna and flora. Demirbas [35] stated that commercial biodiesel fuel has significantly reduced exhaust emissions 75–83% compared to petro-diesel based fuels. Helwani et al. [68] reviewed the technologies for production of biodiesel focusing on green catalytic techniques. The authors reported that combustion of neat biodiesel decreases carbon monoxide (CO) emissions by 46.7%, particulate matter emissions by 66.7% and unburned hydrocarbons by 45.2%. In addition, biodiesel is non-toxic, making it useful for transportation applications in highly sensitive environments, such as marine ecosystems and mining enclosures. Syed et al. [69] reviewed the emission characteristics of biodiesel fuels. The authors revealed the works of many researchers and scientists to agree with the emission reduction from the used of biodiesel compared to petro-diesel fuels.

4.6. Advantages of biodiesel

The application of biodiesel to our diesel engines for daily activities is advantageous for its environmental friendliness over petro-diesel. The main advantages of using biodiesel is that it is biodegradable, can be used without modifying existing engines, and produces less harmful gas emissions such as sulfur oxide [36]. Biodiesel reduces net carbon-dioxide emissions by 78% on a life-cycle basis when compared to conventional diesel fuel [5]. Puppan [70] have discussed the advantages of biofuels over fossil fuels to be: (a) availability of renewable sources; (b) representing CO_2 cycle in combustion; (c) environmentally friendly; and (d) biodegradable and sustainable. Other advantages of biodiesel are as follows: portability, ready availability, lower sulfur and aromatic content, and high combustion characteristics.

5. Application of biodiesel on diesel engines

Biodiesel is a clean burning mono-alkyl ester-based oxygenated fuel derived from natural, renewable and sustainable sources such as vegetable oils, waste cooking oils and animal fats. The physical and chemical properties of biodiesel fuel have been shown to be similar and compatible with those of petro-diesel fuels. Its application on diesel engines has been shown to increase the engine performance and lowers green house gas emissions. The lowering of gas emissions is the biggest advantage of using biodiesel fuel on diesel engines. Avinash [71] stated that increasing industrialization and motorization of the world has led to a steep rise for the demand of petroleum-based fuels. The author also stated that petroleum-based fuels are obtained from limited reserves. These finite reserves are highly concentrated in certain regions of the world. Therefore, those countries not having these

resources are facing energy or foreign exchange crisis, mainly due to the import of crude petroleum. Hence, it is necessary to look for alternative fuels which can be produced from resources locally available within the country such as alcohol, biodiesel, vegetable oils, etc. Ejaz and Younis [59] reviewed the use of biodiesel fuel for compression ignition engines. The authors revealed that scientists and researchers conducted test, using different types of raw and refined oils. The experiments with raw vegetable oils as fuel did not show the satisfactory results, when they were used as raw biodiesel. The fuel showed injector coking and piston ring sticking. Thus, the main conclusion derived by the researchers is that coking is a potentially serious problem with the use of unmodified vegetable biodiesel. However, the refined, chemically processed and degummed vegetable oil mixed with diesel can be used to run compression ignition engine for longer duration. It was also reported that there was a slight decrease in brake power and a slight increase in fuel consumption [59].

5.1. Performance of biodiesel

Demirbas [35] reviewed performance parameters such as brake thermal efficiencies, torque, fuel consumption and power output of biodiesel fuels. Biodiesels are mono-alkyl esters containing approximately 10% oxygen by weight. The author reported that oxygen improves the efficiency of combustion, but it takes up space in the blend and therefore slightly increases the apparent fuel consumption rate observed while operating an engine with biodiesel. Brake thermal efficiency was found to be better in the dual fuel operation and with the methyl ester of Jatropha oil as compared to the blend. It increased from 27.4% with neat Jatropha oil to a maximum of 29% with the methyl ester and 28.7% in the dual fuel operation. Various engine performance parameters such as thermal efficiency, brake specific fuel consumption (BSFC), and brake specific energy consumption (BSEC) can be calculated from the acquired data. The torque, brake power and fuel consumption values associated with CIE fuels were determined under certain operating conditions [35]. Michael et al. [25] showed 18% increases when pure biodiesel from soap-stock and soybean oil were used. These increases are presumably more than the loss of heating value, unless the ester content of biodiesel was unusually low. Contrary, to other few studies conducted only small increases in fuel consumption in some cases no differences between diesel and biodiesel at all noticed. Bettis et al. [72] studied the use of sunflower, safflower and rapeseed oils as liquid fuels. They revealed that the compression engine power output of the fuels is similar to that of diesel fuel, but envisaged long-term durability severe problems due to effects of carbonization. The comparison between sunflower-oil biodiesel and diesel fuels at full and partial loads and at different engine speeds in a 2.5 l 53 kW engine were conducted by Kapilan et al. [67]. They stated that use of biodiesel in diesel engine results in a slight reduction in brake power and a slight increase in fuel consumption. However, the lubricant properties of the biodiesel are better than diesel, which can help to increase the engine life. Also the exhaust emission of the biodiesel is lower than the neat diesel operation due to the presence of oxygen in the molecular structure of the biodiesel. Moreover, the biodiesel fuel is environmentally friendly, because biodiesel does not produce SO_x and also there is no increase in CO_2 emission at global level. Usta [73] use biodiesel from tobacco seed oil to show an increase in torque and power (with a lower heating value of 39.8 MJ/kg). The author conducted several experimental blends with diesel fuel in an indirect injection diesel engine at 1500 and 3000 rpm. Maximum values of torque and power were recorded with a 17.5% blend, inspite of reduced heating value of biodiesel. Lapuerta et al. [66] reported a test of 4.5 l engine with differently oxidized soybean-oil biodiesel fuels. The increase in brake specific fuel consumption (BSFC) with pure biodiesel was 15.1% in the case of oxidized biodiesel (with a peroxide index of 340 meq/kg) and 13.8% in the case of non-oxidized biodiesel. They attributed this difference to the different heating value of both biodiesel fuels. Agarwal and Das [74] conducted different blends on linseed-oil biodiesel with high sulfur diesel fuel in a single cylinder 4 kW portable diesel engine generally used in the agricultural sector and thermal efficiency increases were recorded, especially at low load. On other hand, Lin et al. [75] recorded a decrease in efficiency when palm-oil biodiesel, pure and in 20% blends, were used in a 2.81 indirect injection engine, although the small differences ($<$2.3% in all cases) might be significant to be considered. The authors also reported increases in energy consumption. Kaplan et al. [76] revealed the loss of torque and power ranged between 5% and 10%, and particularly at full load, the loss of power was closer to 5% at low speed and to 10% at high speed.

5.2. Biodiesel higher combustion efficiency

The oxygen content of biodiesel improves and facilitates the combustion process and decreases its oxidation potential. Demirbas [35] reported that the structural oxygen content of a fuel enhances its combustion efficiency due to an increase in the homogeneity of oxygen with the fuel during combustion. Because of this, the combustion efficiency of biodiesel is higher than that of petro-diesel, and the combustion efficiency of methanol/ethanol is higher than that of gasoline and the overall injector coking is considerably low. The author stated that visual inspection of the injector types would indicate no difference between biodiesel fuels and petro-diesel in testing. Charles and Todd [77] concluded that complete combustion converts hydrocarbon fuels to carbon-dioxide and water. Diesel fuel represented by $C_{16}H_{34}$ releases 3.11 kg of CO_2 per kilogram of fuel used in combustion. Biodiesel represented by $C_{22}H_{43}O_2$ releases 2.86 kg of CO_2 per kilogram of fuel used in combustion. Incomplete combustion can result in small amounts of other compounds such as carbon monoxide and aldehydes which eventually also degrade into carbon-dioxide. Syed et al. [69] had reviewed different combustion characteristics such as ignition delay, ignition temperature, and spray penetration of different biodiesel fuels. Peterson et al. [78] reported that carbon-dioxide (CO_2) emissions are significantly lower with biodiesel fuels compared to non-renewable diesel fuels.

6. Conclusion and recommendation

Based on the investigations carried out by several engineers and researchers, the following conclusions and recommendations were made:

1. The application of membrane technology for the separation and purification of biodiesel was discovered to give better results compared to the conventional technologies.
2. It was observed that high purity and quality biodiesel is necessary to avoid compression ignition engine problems.
3. The purity of raw materials for the development of biodiesel fuel was found to be crucial for the success of its application and future replacement of non-renewable fossil fuels.
4. Biodiesel fuel has been reported to provide a lot of potentials than fossil fuel for instance better quality gas exhaust generation which can lead to reduction in global warming effects and environmental hazards.
5. The performance parameters of biodiesel proved to surpass that of diesel fuel and its application requires no engine modification.

6. The development of biodiesel should be encouraged to create jobs opportunities and increase earnings to the populace especially in communities where these raw materials are produced.

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